PARAXYLENEDISULPHONIC ACID

A DISSERTATION

PRESENTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

JESSE H. HOLMES.

1890.

BALTIMORE:
PRESS OF ISAAC FRIEDENWALD,
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Introduction.[1]

The following paper includes a discussion of the preparation and properties of one of the disulphonic acids of paraxylene, certain of its derivatives, and the oxidation products of its amide. The material used in the experiments was prepared in several portions and by slightly differing methods, and the products were obtained in two modifications. Whether the differences are due to conditions merely physical, or involve difference in chemical constitution, has not been determined.

The sulphonic acids have been too long and too generally known among chemists to require any general comment here. Concerning those of the aromatic series, however, in which two sulphonic acid groups are present, a few words will not be inappropriate, and an outline of work done and conclusions reached concerning the course of oxidation in negative substitution products of certain aromatic compounds is essential to an understanding of the purposes and conclusions of the work to be described.

Disulphonic Acids.

As with other di-substitution products of benzene, the existence of three isomeric disulphonic acids might be predicted. The first of which we have record is that made by Buckthorn and Hofmann,[2] by long-continued treatment of sulphanilic acid with fuming sulphuric acid. This was shown by Limpricht[3] to be the meta compound. Barth and Senhofer[4] have shown that both meta and para disulphonic acids are formed by heating benzene with fuming sulphuric acid. If the temperature is kept down and the heating is not too long continued, the product is chiefly the meta acid.

Parabenzenedisulphonic acid was prepared by Garrick[5] in 1869, and by R. Brunner[6] in 1871. The former treated benzenesul-

[1] The work of which an account is given in this dissertation was undertaken at the suggestion of Professor Remsen, and has been carried on under his constant supervision. It gives me pleasure to express here my appreciation of his uniform kindness and consideration.

[2] Ann. Chem. (Liebig) **100**, 164. [3] Ber. d. chem. Ges. **9**, 551. [4] Ibid. **8**, 1477.

[5] Zeitsch. Ch. 1869, 549. [6] Ber. d. chem. Ges. **4**, 984.

phonic acid with fuming sulphuric acid, the latter with sulphuric anhydride. The constitution of these products was determined by v. Richter[1] in 1872.

The ortho acid was made by Drebes,[2] a pupil of Limpricht's, in 1876, by the action of fuming sulphuric acid on meta-amidobenzenesulphonic acid and subsequent removal of the amido group by the diazo reaction and alcohol.

A point of interest with all of these acids is that, in most cases, it has been found very difficult to obtain from them well-crystallising salts or other derivatives.

Of toluenedisulphonic acids, six are possible according to the Kekulé theory of benzene, and that number is known. The most important discussion of these compounds is that of P. Klason,[3] who, in 1886–7, discovered the sixth isomer and determined its constitution as well as those of three others already known. The constitutions of the remaining two had been previously worked out.

Ortho-ortho(1-2-6)-toluenedisulphonic acid was first made by Kornatzki,[4] by the action of fuming sulphuric acid and its anhydride on parabromtoluene. The bromine was removed by treatment with sodium amalgam.

One of the two ortho-meta compounds (1-2-3) was first prepared by Limpricht and Richter.[5] They treated paratoluidinemetasulphonic acid with fuming sulphuric acid and chlorsulphuric acid, afterwards removed the amido group in the usual way. The same acid was obtained by Klason,[6] together with the other ortho-meta compound (1-2-5), by heating metatoluidinesulphonic acid with fuming sulphuric acid at 180°.

The second ortho-meta-toluenedisulphonic acid (1-2-5) was obtained by Hakansson,[7] together with a much larger quantity of the para-ortho (1-2-4) isomer, by the direct action of fuming sulphuric acid on orthotoluenesulphonic acid at 160°. It was called by him the β-acid, while the more abundant product was known as the α-acid. The same ortho-meta compound (1-2-5) was prepared also by Klason[8] in a manner which showed its constitution. Orthotoluidinemetasulphonic acid (1-2-5) was changed by the action of nitrous acid to the diazo compound, and this to the cor-

[1] Ber. d. chem. Ges. **5**, 422. [2] Ibid. **9**, 553. [3] Ibid. **8**, 1477.
[4] Ann. Chem. (Liebig) **221**, 191. [5] Ber. d. chem. Ges. **18**, 2177. [6] Loc. cit.
[7] Ber. d. chem. Ges. **5**, 1084. [8] Loc. cit.

responding thiocresol by potassium sulphydrate. The hydrosulphide group was then oxidised to the sulphonic acid group, and the resulting product was shown to be identical with that prepared as explained above. The reactions may be graphically represented as follows:

$$C_6H_3\begin{cases}CH_3 & (1)\\ NH_2 & (2)\\ SO_3H & (5)\end{cases} \rightarrow C_6H_3\begin{cases}CH_3\\ SH\\ SO_3H\end{cases} \rightarrow C_6H_3\begin{cases}CH_3\\ SO_3H\\ SO_3H.\end{cases}$$

The ortho-para acid (1-2-4) was made by Blomstrand,[1] by direct action of fuming sulphuric acid on toluene or on ortho- or paratoluenesulphonic acid. Senhofer[2] obtained the same substance by heating toluene to 230° in a sealed tube with sulphuric acid and phosphorus pentoxide. In 1880, Fahlberg[3] made this compound by treating orthotoluenesulphonchloride with sulphuric acid. In the next year he also determined its constitution,[4] his results agreeing entirely with the conclusions of Klason.

The fifth acid, the meta-meta (1-3-5) compound, was made by Limpricht and Hasse[5] from orthotoluidinemetasulphonic acid.

Finally the meta-para (1-3-4) acid was prepared by Klason[4] through the corresponding thiocresol of metatoluenesulphonic acid, as in the case of the 1-2-5 acid.

Only in a few cases can well-crystallised derivatives be obtained from these acids. Either they are so soluble that they can only be obtained by evaporating their solutions nearly or quite to dryness, or they crystallise on cooling the concentrated solution, in very imperfect forms. The same fact has been observed in working with xylenedisulphonic acid. The acid salts could not be obtained at all so far as attempted, and the neutral salts are nearly all amorphous.

PARAXYLENEDISULPHONIC ACID, $C_6H_2\begin{cases}CH_3\\ SO_3H\\ CH_3\\ SO_3H\end{cases}$.

This acid was prepared according to the method by which Fahlberg made toluenedisulphonic acid, by treating xylenesulphon chloride with strong sulphuric acid. The details of the operation were as follows: About thirty-five grams of pure para-

[1] Ber. d. chem. Ges. **5**, 1084. [2] Ibid. **5**, 333. [3] Ibid. **12**, 1050; Am. Chem. J. **1**, 174.
[4] Am. Chem. J. **2**, 181. [5] Ber. d. chem. Ges. **18**, 2177.

xylene, boiling at 136°–138°, were gradually added,with constant shaking, to about twice the volume of fuming sulphuric acid diluted with a small quantity of ordinary acid. The dilution was found necessary in order to avoid blackening the product; and in spite of it the sulphonic acid obtained was dark-colored. Action takes place readily. In the early stages of the operation it was necessary to cool the mixture in water, and at last some warming is necessary to complete the reaction. After cooling the mixture, a small quantity of water was added, when the sulphonic acid crystallised out;[1] on further dilution it redissolved. The solution was now diluted to four or five liters, the excess of sulphuric acid precipitated with chalk, the gypsum carefully washed with hot water, and the solution of calcium xylenesulphonate evaporated to about two liters. The calcium salt was now transformed into the sodium salt by the addition of a slight excess of sodium carbonate, the precipitated calcium carbonate separated by filtration, and the sodium salt solution evaporated to dryness. The sodium salt, after drying, was quite dark-colored. It was treated with an equal weight of phosphorus pentachloride, and then, as the reaction did not seem to be complete, with a considerable excess. It was found later that the yield was very unsatisfactory unless this excess was used, although every precaution was taken to have the salt perfectly dry. The action with the pentachloride took place at once, and after the evolution of hydrochloric acid ceased the semi-liquid mass was heated for some time on a water-bath, to drive off the oxychloride of phosphorus. On adding a large volume of water, xylenesulphon chloride separated as a dark, turbid, oily liquid, which did not entirely solidify even when cooled in a freezing mixture. According to Jacobsen[2] this chloride, when pure, is a crystalline solid melting at 24°–26°.

The chloride was now treated with four or five times its volume of fuming sulphuric acid. Hydrochloric acid escaped at once and, on heating, the evolution of this gas continued for some time. The heating was continued until a drop of the mixture showed no turbidity when dropped into water, this being an indication that the acid chloride was completely decomposed. The acids were now diluted and neutralised with calcium carbonate. The sodium salt was prepared as before and was treated with twice its weight of phosphorus pentachloride. After removing the phosphorus

[1] Ber. d. chem. Ges. **10**, 1009. [2] Ibid. **10**, 1009.

oxychloride by evaporation, the disulphon chloride was separated in several liters of water.

XYLENEDISULPHON CHLORIDE, $C_6H_3\left\{\begin{matrix}(SO_2Cl)_2\\(CH_3)_2\end{matrix}\right.$.

In the impure state, as at first obtained, the disulphon chloride was a tarry, brownish-yellow mass which adhered strongly to filter-paper, glass, etc. It solidifies easily when cooled in a freezing mixture. Considerable difficulty was encountered in finding a suitable solvent from which to crystallise it. It dissolves quite readily in cold alcohol, but cannot be obtained again therefrom, probably breaking down to the corresponding disulphonic acid. It is rather easily soluble in benzene, chloroform, acetone, and glacial acetic acid, but does not crystallise from any of them. When the benzene solution is evaporated to dryness the chloride is left as a transparent, varnish-like cake in the bottom of the beaker, which, on standing, draws together into something like crystalline structure, still containing, of course, all the original impurities. Ordinary benzene was finally found to be the most satisfactory solvent. The chloride is dissolved in it by boiling in a water-bath, and the solution is allowed to cool very slowly, when the crystals separate in radiating bunches of considerable size.

After a single recrystallisation the chloride was white and appeared to be perfectly pure. The melting point was 72°–74°. On standing in contact with the air the crystals turn slightly yellow. The substance was analysed for chlorine by the method of Carius. As preliminary experiments showed it to decompose very easily, the tube was heated only to about 100°.

.2652 gram of xylenedisulphon chloride gave .2527 gram of silver chloride.

		Calculated.	Found.
$C_8H_8O_4S_2$	232	76.57	...
2Cl	71	23.43	23.56
	303	100.00	

An attempt was made to discover the crystal system and constants, but the planes were found to be so imperfect that the angles could not be accurately measured.

Xylenedisulphonic Acid, $C_6H_2(CH_3)_2(SO_3H)_2$.

The quantity of chloride prepared as just described was now divided into two parts. The larger portion was transformed into the disulphamide, which will be spoken of later. The remainder was boiled with water for about twelve hours, in a flask connected with an inverted condenser. At the end of this time a small quantity of organic matter remained undissolved, which was not further affected by boiling water. It dissolved easily when warmed with alcohol and apparently decomposed. The quantity was too small for any careful investigation.

The solution containing the decomposed chloride was now evaporated to dryness on a water-bath, the residue redissolved and the evaporation repeated until no more hydrochloric acid was given off. The disulphonic acid was then dissolved again in water and the solution was treated several times with animal charcoal, being finally obtained clear with slight yellow tinge. On evaporation to small volume the acid crystallises out in needles which are exceedingly soluble in water.

Barium Xylenedisulphonate, $C_6H_2(CH_3)_2(SO_3)_2Ba$.

A solution of xylenedisulphonic acid was boiled with pure barium carbonate and filtered from the excess of the latter. A perfectly clear, colorless solution was obtained. On evaporation the salt is precipitated in the form of brownish scales which show some signs of crystalline structure under the microscope. It was found impossible to obtain it in good crystals, though it is rather less soluble than the other salts of the same acid. The salt contained no water of crystallisation. Analysis resulted as follows:

I. .2825 gram of salt gave .1621 gram of barium sulphate.

II. .2498 gram of salt gave .1443 gram of barium sulphate.

		Calculated.	Found. I.	Found. II.
$C_8H_8O_6S_2$	264	65.84	...	...
Ba	137	34.16	33.74	33.97
	401	100.00		

The analysis as well as the color showed that the substance was not entirely pure.

CALCIUM XYLENEDISULPHONATE, $C_6H_2(CH_3)_2(SO_3)_2Ca + 4H_2O$.

The calcium salt was made by neutralising the solution of free acid with finely powdered Iceland spar. On evaporating to a small volume and allowing to stand, the salt crystallised out in tablets nearly square and with beveled edges. An approximate measurement of their angles indicated that they belonged to the triclinic system, though approaching the symmetry of the tetragonal system. The crystals are biaxial, and are cut by the plane of the optic axis very nearly or quite in the direction of the shorter diagonal.

The calcium salt is very soluble in water, dissolving easily if the solution from which it crystallises is slightly warmed. If the solution is concentrated beyond a certain point the salt is decomposed slowly and fine needle-shaped crystals of gypsum are deposited. One of the four molecules of water of crystallisation could not be driven off without decomposition of the salt. The partially dried salt, which falls apart as a fine powder, is very hygroscopic, taking up water even from calcium chloride in a desiccator. This property seems to be common to a number of the salts of this acid, so that determinations of water are, at best, only approximate. While standing on the balance-pan, water is absorbed so rapidly as to prevent accurate determinations.

Analysis resulted as follows:

I. .3521 gram of the salt lost .0524 gram of water at 200° and gave .1272 gram of calcium sulphate.

II. .2327 gram gave .0840 gram of sulphate.

III. .1377 gram of salt lost .0199 gram of water and gave .0500 gram of sulphate.

		Calculated.	Found. I.	II.	III.
$C_8H_8O_6S_2H_2O$	282	75.00	...	...	...
$3H_2O$	54	14.36	14.88	...	14.45
Ca	40	10.64	10.64	10.62	10.64
	376	100.00			

The rest of the salts of xylenedisulphonic acid were made from another stock of material prepared in the same general way, but some slight differences were introduced into the method of preparation, which are noted here because the acid obtained differed in some particulars from that previously made. The chief dif-

ferences in the process were that the temperature was kept lower in both treatments with sulphuric acid than in the first case, and the transformation from xylenesulphon chloride to xylenedisulphonic acid was accomplished by the use of sulphuric acid of specific gravity 1.84 instead of the fuming acid. The blackening of the material was thus avoided and colorless products were obtained throughout the operations. The differences observed between the two products were not very great and may have been due to slight impurities in the first. The two chlorides show the same melting point—about 72°—but the crystal form of the specimen last prepared was apparently different, the crystals appearing from the benzene solution as thin rectangular plates, instead of showing a prismatic habit as did the first product. The second stock of the acid itself could not be obtained in crystalline form, while the first crystallised in needles. The amide last prepared showed some slight differences, which will be mentioned when the discussion of that substance is reached. The calcium salt, which crystallised well, though not easily, in the first instance, could not be made to crystallise in the second, but separated from the solution as an amorphous precipitate on sufficient concentration. The second lot of acid was found to contain a small quantity of sulphuric acid. It was purified by making the lead salt and decomposing its solution by action of hydrogen sulphide.

LEAD XYLENEDISULPHONATE, $C_6H_2(CH_3)_2(SO_3)_2Pb.3H_2O$.

The lead salt was prepared by dissolving lead carbonate in a dilute solution of the acid. It was found impossible to crystallise it, but it was obtained in an amorphous condition by evaporating the solution to small volume. The salt is slightly soluble in alcohol, and when this solution is evaporated nearly to dryness the salt crystallises in long, lustrous but indistinct filaments; so small a quantity goes into solution, however, that this method is not available for purification. As in the case of the crystalline calcium salt, the last molecule of water of crystallisation cannot be driven off without decomposing the compound.

The following results were obtained by analysis:

I. .1280 gram gave .0096 gram of water and .0742 gram of lead sulphate.

II. .2485 gram gave .1438 gram of lead sulphate.

III. .2156 gram lost .0154 gram of water.

		Calculated.	Found. I.	II.	III.
$C_8H_8O_6S_2.H_2O$	282	53.79	...	...	...
$2H_2O$	36	6.86	7.50	...	7.14
Pb	206.4	39.35	39.52	39.53	...
	524.4	100.00			

Magnesium Xylenedisulphonate, $C_6H_2(CH_3)_2(SO_3)_2Mg.7H_2O$.

This salt was prepared by dissolving magnesium oxide in a solution of the free acid. Like the other salts mentioned, it is very soluble and cannot be crystallised. It was obtained as an amorphous precipitate. As before, the water of crystallisation could not be driven off without decomposing the salt. While it is evident that, calculating the amount of water of crystallisation from the determination of the base alone is not a safe method, yet the results for the latter are so sharp that they are given for what they are worth. The attempt to drive off water was made twice and persevered in until the salt blackened. 18.74 and 18.63 per cent. of water were driven off in these two experiments, while the amount required to correspond with the amount of base present is above thirty per cent.

I. .2904 gram of the salt gave .0853 gram of magnesium sulphate.

II. .2934 gram lost .0550 gram of water and gave .0861 gram of magnesium sulphate.

III. .1819 gram lost .0339 gram of water and gave .0525 gram of magnesium sulphate.

		Calculated.	I.	Found. II.	III.
$C_8H_8O_6S_2.7H_2O$	390	94.20	...	...	...
Mg	24	5.80	5.87	5.86	5.87

The amounts of magnesium calculated for the weight of the salt after driving off as much water as possible, are as follows:

II. .2384 gram of dried salt gave .0861 gram of magnesium sulphate.

III. .1319 gram of salt gave .0535 gram of sulphate.

		Calculated.	Found. II.	III.
$C_8H_8O_6S_2$	264	91.67	...	...
Mg	24	8.33	7.22	7.19
		100.00		

SILVER XYLENEDISULPHONATE, $C_6H_2(CH_3)_2(SO_3Ag)_2.H_2O$.

The silver salt was prepared by dissolving pure silver oxide in a solution of the acid. After several attempts it was obtained in crystalline form as small scales with a pearly luster. On exposure to light it blackens. Only a very small quantity was made. Analysis resulted as follows:

.1319 gram of silver salt lost .0049 gram of water and yielded .0571 gram of silver.

		Calculated.	Found.
$C_8H_8O_6S_2$	264	...	...
H_2O	18	3.62	3.71
2Ag	215.3	43.29	43.29
	257.3		

Discussion of the probable constitution of xylenedisulphonic acid will be given after the experiments on the oxidation of its amide have been described.

XYLENEDISULPHONAMIDE, $C_6H_2(CH_3)_2(SO_2NH_2)_2$.

As stated above, the main portion of xylenedisulphon chloride was transformed into the amide. That obtained from the first preparation will be described first, and the points of difference in the second preparation will be pointed out later.

The chloride, after being dried as completely as possible, was treated with strong ammonia, and the mixture was evaporated to dryness on the water-bath. The chloride turns yellow when first treated with the ammonia, but gradually loses this color and becomes nearly white. It was found better, after some experiments, to pass gaseous ammonia, obtained by warming its concentrated solution, over the dry chloride contained in a flask. The reaction seemed to be complete, though it was thought best to treat the amide so prepared with a small quantity of the ammonia solution before proceeding. After thorough washing

with cold water the amide appeared as a fine light-gray powder. It is very difficultly soluble in water, more easily in a mixture of alcohol and water. It dissolves readily in alkalis, and is reprecipitated by acids as a flocculent white mass. Pyridine dissolves it in large quantities, but deposits it on evaporation or dilution as an amorphous precipitate. It is only slightly soluble in glacial acetic acid, chloroform, and ether. Acetone dissolves it readily, as does also a mixture of acetone with a large proportion of water, but it cannot be crystallised from such a solution. It was finally found best to dissolve the substance in a mixture of about equal parts of alcohol and water, purify by boiling with animal charcoal, boil off most of the alcohol, and crystallise from a large volume of water. On allowing the solution in alcohol and water to cool, the disulphonamide appears in extremely small satiny crystals which do not settle even on long standing. When the mixture is stirred the amide in suspension presents a very remarkable appearance, due to the varying reflections from the minute crystal surfaces. The crystals obtained from the solution in water are larger, but are still too small to be distinguished by the naked eye. As seen under the compound microscope, they are found to consist of very thin tabular plates which, in polarised light, show a complicated twinned structure. These plates show parallel extinction, and the characteristic plane angles are 60° and 30°, as nearly as they can be measured on the revolving stage of the microscope. A considerable number of different shapes were observed, the thin plates having three, four and six sides. The crystals appeared to be optically biaxial, but on account of the extreme thinness of the plates this could not be certainly determined.

On evaporating the mother-liquors from these crystals, a white flocculent substance was obtained which resembles the amide in some particulars, but settles more readily. A partial analysis indicated that it had the same composition, but was less pure.

An attempt was made to determine the melting point of the disulphonamide in a sulphuric acid bath, but it was found not to melt below the boiling point of the acid used. It was then determined in an air-bath made by enclosing a small test tube in a larger one, leaving a considerable layer of air between. This device was found very convenient in determining high melting points. The disulphonamide melts with partial decomposition at 294°–295°.

Analysis of the crystallised substance gave the following results:

Sulphur, determined by Pearson's method:

I. .1882 gram gave .3307 gram of barium sulphate.

II. .1703 gram gave .2988 gram of barium sulphate.

Nitrogen, determined by Kjeldahl's method as modified by Gunning:

I. .1778 gram gave .0186334 gram nitrogen.

II. .3240 gram gave .0337456 gram nitrogen.

III. .2282 gram gave .0248837 gram nitrogen.

Carbon and hydrogen, determined by combustion with lead chromate and lead oxide:[1]

I. .2004 gram yielded .2687 gram of carbon dioxide and .0928 gram of water.

II. .1606 gram gave .2150 gram of carbon dioxide and .0738 gram of water.

		Calculated.	Found. I.	II.	III.
C_8	96	36.36	36.56	36.50	...
H_{12}	12	4.55	5.14	5.12	...
S_2	64	24.24	24.15	24.02	...
N_2	28	10.61	10.48	10.41	10.90
O_4	64	24.24			
	264	100.00			

The disulphonamide from the second stock of material possessed the same general properties as that from the first, including the melting point. A sulphur determination after a single crystallisation indicated that it was not entirely pure. After several recrystallisations some of the crystalline product was obtained, but the larger part resembled the flocculent substance obtained from the mother-liquors of the first crystallised amide. It was not determined whether these differences were due to the presence of an isomeric disulphonamide or merely to impurities.

The oxidation of the disulphonamide was next undertaken. A brief review of the work already done in this line will be given here.

Oxidation of Substitution Products.

Since 1879 a series of experiments has been carried on at the Johns Hopkins University Laboratory and under the direction of

[1] Method as modified by R. R. De Roode, Am. Chem. J. **12**, 220.

Professor Remsen, with the object of determining the effects of negative substituting groups on the course of oxidation of the homologues of benzene. The oxidising agents used have been potassium dichromate and potassium permanganate.

Isolated examples of the effect of negative substituting groups are mentioned by various chemists previous to this time. These are summed up in a preliminary article by Professor Remsen,[1] which also points out the general direction to be taken in the experiments which follow. Beilstein and Kreusler[2] found that the presence of a nitro-group or of chlorine in xylene prevented the oxidation of one of the methyl groups; and that dinitrotoluene is only slightly attacked by oxidising agents, while nitrotoluene is readily oxidised to paranitrobenzoic acid. Vollrath[3] showed that chlorparaxylene yields on oxidation chlorparatoluic acid, and bromine was found a little later to have a similar effect as a substituting agent. Remsen[4] observed that paratoluenesulphonamide is more readily oxidised than the corresponding ortho compound. This observation led him to suspect that the negative group in the ortho position exerts a protective influence on the oxidisable group, both in this and in other cases; and the experiments which followed were intended to furnish evidence on this point.

These experiments included study of the oxidation by potassium dichromate of substitution products of toluene, the xylenes, paraethyltoluene, cymene and mesitylene. The results are stated as follows: "In all cases now on record, in which hydrocarbon residues are shown to be protected from oxidation by the presence of negative groups, the latter are in the ortho position with reference to the former; whereas oxidisable residues situated either in the meta or para position with reference to the negative group, are, under the same circumstances, transformed just as if the negative group were not present."[5] This statement applies, of course, only to oxidation by potassium dichromate.

It was observed in a number of cases that the product of oxidation with chromic acid was further oxidised by potassium permanganate, showing that, under some conditions at least, the methyl group in the ortho position with reference to a negative group is not protected from oxidation by that reagent. This led to a further investigation of the action of permanganate on

[1] Am. Chem. J. **1**, 32. [2] Ann. **144**, 168. [3] Ibid. **144**, 266.
[4] Ibid. **178**, 275. [5] Am. Chem. J. **1**.

oxidising substitution products. It was found that orthotoluenesulphonamide[1] is readily attacked by it, but, instead of orthosulphaminebenzoic acid, a substance was obtained whose formula differed from it by the subtraction of the elements of one molecule of water. The evidence at command shows that the water is probably eliminated from the carboxyl and amido groups in such a way as to cause union between the carbon of the former and the nitrogen of the latter:

$$C_6H_4\begin{cases} CO\ OH \\ SO_2NH\ H \end{cases} \longrightarrow C_6H_4\begin{cases} CO \\ SO_2 \end{cases}\!>\!NH.$$

The name "benzoic sulphinide" was given to this substance; and as other compounds of similar nature were discovered, the name "sulphinide" was given to compounds containing the group $\begin{matrix} CO \\ SO_2 \end{matrix}\!>\!NH$. The sulphinides are weak monobasic acids, the imido hydrogen being replaceable by metals. Experiments with a large number of substances indicate the truth of the following statement: "Whenever a compound containing the sulphamide group, with methyl in the ortho position, is oxidised by potassium permanganate in alkaline solution, a sulphinide is formed." If the solution is kept neutral or acid, the corresponding sulphonic acid is formed.

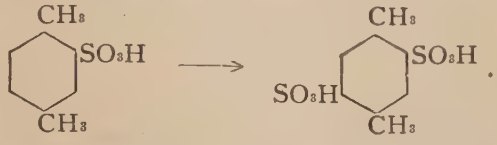
In the case of mesitylenesulphonamide a sulphinide is obtained by oxidation with potassium dichromate in acid solution.[2] The oxidised group is therefore probably in the ortho position with reference to the sulphamide groups, and the course of the reaction is thus different from what would be expected. Such negative groups as the nitro group, chlorine and bromine, on the other hand, protect the two methyl groups of mesitylene which are in the ortho position, and allow the oxidation of the group in the para position, when dichromate is the oxidising agent.

Some experiments by Remsen and Palmer[3] seemed to indicate that on oxidation of substitution products containing only a single oxidisable group, the methyl in the ortho position from the sulphonamide group is more readily oxidised by permanganate in alkaline solution than the isomeric meta and para compounds, these facts being just the reverse of those noticed by Professor Remsen when dichromate is the oxidising agent employed.

[1] Am. Chem. J. **1**, 417. [2] Ibid. **2**, 130 [3] Ibid. **4**, 147.

Some unpublished results obtained in 1889 by K. Shimomura do not altogether confirm Palmer's observations, the former indicating that unless the solution is very strongly alkaline the para compound is more rapidly oxidised than the ortho compound.

Although nothing was known as to the position which would be taken by the second sulphonic acid group in the formation of xylenedisulphonic acid, it seemed probable, from the analogies of similar compounds, that it would take the para position with reference to the first sulphonic acid group, and thus the ortho position as regards the second methyl group.



In this case the oxidation of the two methyl groups would probably yield a disulphinide, or a substance in which the group $\begin{matrix} CO \\ SO_2 \end{matrix}>NH$ would occur twice. The formation of this substance was the objective point of this investigation.

Oxidation of Paraxylenedisulphamide.

In the first experiment a very large excess of both permanganate and alkali was used. The proportions taken were:

Disulphonamide, ...	5 grams.
Potassium permanganate, ...	40 "
Potassium hydroxide, ...	10 "
Water, ...	1 liter.

These were heated in a water-bath and by the introduction of a current of steam for about four hours. The excess of permanganate was then precipitated by alcohol, the filtrate from the hydroxides of manganese was brought nearly to neutrality by hydrochloric acid and was then evaporated on the water-bath to about 100 cc. On acidifying, after allowing the solution to cool, a considerable precipitation of a fine crystalline substance occurred. This settled at once and filtered easily. After several recrystallisations it seemed perfectly pure. When heated on platinum foil it left a considerable alkaline residue, which was shown by the flame-test to contain potassium. A test for the presence of nitrogen

was made by fusing the substance with sodium, heating to a high temperature, dissolving the product in water, and adding solutions of ferrous and ferric salts. This test gave negative results. As the method has been shown to be unsatisfactory in the analysis of some compounds containing sulphur, a quantitative determination of nitrogen was undertaken, which proved that element to be present in considerable quantity. A partial analysis of the substance was made, which will be discussed a little later.

After some further experiments as to the best proportions of reagents, the rest of the amide of the first stock was oxidised, using the proportion of permanganate calculated for the oxidation of the two methyl groups:

Disulphonamide, ...	20 grams.
Potassium permanganate, ...	48 "
Potassium hydroxide, ...	10 "
Water, ...	2½ liters.

This solution was heated in a water-bath until it was completely decolorised. The filtrate was then concentrated *after* being acidified with hydrochloric acid. On cooling, little rosettes of white crystals appeared, and later, some of the potassium compound mentioned above.

Disulphamineparatoluic Acid, $C_6H_2(CH_3)(SO_2NH_2)_2COOH.H_2O$.

The main product was repeatedly crystallised, but could not be obtained in sharp crystals. It comes out always in arborescent radiating filaments. Its melting point, determined in an air-jacket, was about 272°. It burns on platinum foil, leaving no residue. Titration with standard ammonia shows it to be a monobasic acid. At 105° it loses one molecule of water of crystallisation. Analysis resulted as follows:

.1639 gram of the acid lost .0095 gram of water at 105°.

$C_8H_{10}O_6S_2N_2$	294	94.23	...
H_2O	18	5.77	5.79
	312	100.00	

.1639 gram of acid on combustion gave .0586 gram of water and .1835 gram of carbon dioxide.

.1116 gram gave .0094781 gram of nitrogen.
.1509 gram gave .2277 gram of barium sulphate.

		Calculated.	Found.
C_8	96	30.77	30.53
H_{12}	12	3.85	3.97
N_2	28	8.97	8.49
S_2	64	20.51	20.72
O_7	112	35.90	...
	312	100.00	

It was thought that the potassium salt mentioned above might be the potassium salt of this acid, being precipitated by acids without decomposition in the cold because of its comparative insolubility. A small quantity was boiled with hydrochloric acid, and on cooling an insoluble acid was precipitated, which on recrystallisation resembled the acid oxidation product, but did not melt at exactly the same point. The percentages of sulphur and nitrogen agree in indicating that the potassium compound is the salt of the acid in question with two molecules of water of crystallisation. At 150° only five-tenths of one per cent. of water was lost; but many substances containing the two sulphamine groups retain their water of crystallisation to a higher temperature. On account of lack of materials more attempts to drive off the water were not made. It was supposed when the analyses were made that all the water was driven off, a constant weight being reached. The analyses resulted as follows:

I. .1938 gram gave .0450 gram of potassium sulphate.
II. .1736 gram gave .0404 gram of potassium sulphate.
I. .2086 gram gave .0165353 gram of nitrogen.
II. .1630 gram gave .01240528 gram of nitrogen.

		Calculated.	Found. I.	Found. II.
$C_8H_9O_6S_2.2H_2O$	301	81.81	...	...
K	39	10.59	10.41	10.43
N_2	28	7.60	7.92	7.65

Sulphur determinations varied so widely that they were considered of no value. It is not thought that the evidence as to the composition of this salt is at all conclusive, but it is favorable to the view stated.

Barium Disulphaminetoluate, $C_6H_2(CH_3)(SO_2NH_2)_2COOba.2\frac{1}{2}H_2O$.

The barium salt was obtained by dissolving barium carbonate in an aqueous solution of the purified acid. The two samples analysed were made from different preparations of the acid. The salt is exceedingly soluble. It appears from the much concentrated solution in little, warty, spherical masses which are quite hard. These were dried between filters, reduced to fine powder and again pressed between filter papers. Analysis resulted as follows:

I. .1539 gram of salt gave .0149 gram of water at 130° and .0442 gram of barium sulphate.

II. .1810 gram lost .0227 gram of water with slight decomposition at 240°, and gave .0523 gram of barium sulphate.

			Found.	
		Calculated.	I.	II.
$C_6H_9O_6N_2S_2$	295	72.21	...	...
$2\frac{1}{2}H_2O$	45	11.02	9.68	11.15
$Ba_{\frac{1}{2}}$	68.5	16.77	16.88	16.99
		100.00		

The results in this case are not satisfactory, but the composition assigned seems to be justified by the facts. In the second water determination, after the weight was taken the crucible and salt were left in a desiccator over calcium chloride for the night. The next morning the weight showed that enough water had been taken up to reduce the percentage removed from 11.15 to 9.45 per cent., which last is about the same quantity that remained when the salt was dried at 130°. On account of the extreme solubility of the salt it could not be purified by recrystallisation, which accounts in part for the inconclusive results as to the basic constituent.

Calcium Disulphaminetoluate, $C_6H_2(CH_3)(SO_2NH_2)_2COOca$.

The calcium salt was prepared from finely powdered Iceland spar. On evaporating the solution to small volume and allowing to cool, the whole solidifies to a stiff, transparent, jelly-like mass which could be removed from the beaker as from a mould. No attempt was made to dry it for analysis.

Lead Disulphaminetoluate, $C_6H_2(CH_3)(SO_2NH_2)_2COOpb.3H_2O$.

This salt was prepared by dissolving lead carbonate in a solution of the free acid. It crystallises out on cooling the solution in long, lustrous needles which show a tendency to arrange themselves in fan-shaped aggregates. Analysis resulted as follows:

.1652 gram of the salt lost .0203 gram of water and gave .0551 gram of lead sulphate. There was a slight yellowing at the end of the water determination, which probably accounts for the high result.

		Calculated.	Found.
$C_6H_9O_6N_2S_2$	295	65.24	...
$3H_2O$	54	11.94	12.28
Pb_1	103.2	22.82	22.76
	452.2	100.00	

Silver Disulphaminetoluate, $C_6H_2(CH_3)(SO_2NH_2)_2(COOAg)_2.2H_2O$.

The silver salt was prepared by first making the neutral ammonium salt, an excess of ammonia being added to the acid solution for that purpose. The excess was driven off by evaporation and the silver salt was then precipitated by the addition of silver nitrate. It crystallises on cooling in very fine needles which have a tendency to fan-shaped arrangement, as in case of the lead salt. It is less soluble than the lead salt. A few drops of its solution added to a large volume of cold water render it milky. It decomposes with blackening on exposure to light and air when in a moist condition. It was dried between filter papers and analysed with the following results:

.1563 gram lost .0130 gram of water at 180° and gave .0386 gram of silver.

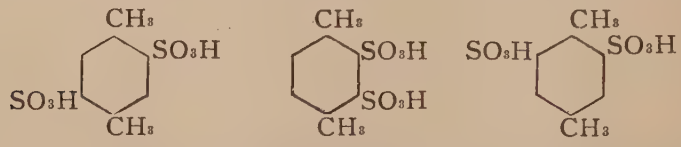
		Calculated.	Found.
$C_8H_9O_6N_2S_2$	295	67.20	...
$2H_2O$	36	8.20	8.32
Ag	108	24.60	24.69
	439	100.00	

The products of oxidation of the second preparation of xylene-disulphamide showed the presence in small quantity of one sub-

stance not observed in the previous experiments. This consisted of crossed and radiating crystals with distinct angles. They were transparent, and differed markedly from disulphaminetoluic acid. The melting point is about 274°. It loses no water on heating to 105°. Enough crystals were picked out for a partial analysis, which showed the presence in the compound of 10.35 per cent. of nitrogen and 24.28 per cent. of sulphur. The original disulphamide of which this is an oxidation product contains 10.60 per cent. of nitrogen and 24.24 per cent. of sulphur, but does not at all resemble the substance in question. Sufficient time and material were not at disposal to allow a further investigation.

Conclusion.

Plainly, the evidence obtained by the oxidation of xylenedisulphamide, as described, is not sufficient to allow any final decision as to the constitution of the disulphonic acid in question. Since, however, in all recorded cases a methyl group and a sulphamide group in the ortho relation yield a sulphinide on oxidation by permanganate, it seems probable that such a relation did not exist between the methyl group oxidised and either of the sulphamide groups of the disulphamide. There are three possible arrangements of the two sulphonic acid groups as introduced into the molecule of paraxylene, which may be represented as follows:



In two of these, each methyl group is in the ortho relation with a sulphonic acid radical. In the third, however, the two radicals occupy the two ortho positions with reference to a single methyl group, leaving the other in the meta position as regards both of them. It seems probable, therefore, that this represents the constitution of the compound studied, and that the two negative groups protect the ortho-methyl groups from oxidation.

BIOGRAPHICAL.

I was born at West Liberty, Iowa, January 5, 1864.

I was educated in the public schools of the town, being graduated from the High School in 1879. My college education was obtained in the Nebraska State University between 1879 and 1885, including one year of post-graduate study, during which I occupied the position of Assistant Librarian. My course included the regular studies of the scientific department and most of those of the literary department, and led to the degree Bachelor of Science.

I entered the Johns Hopkins University in 1885, spending the ensuing year in analytical work under the direction of Dr. Morse. During the year I also attended lectures by Professor Remsen and by Drs. Williams, Kimball and Morse. For the next two years I was engaged in teaching at the Friends' Select School in Washington, D. C., and spent the summers in botanical work under the U. S. Department of Agriculture.

The two years just past have been spent in the study of chemistry in the Johns Hopkins chemical laboratory, and of typical forms of life in the biological laboratory. I have also attended lectures by Professors Remsen and Martin, and by Drs. Williams and Renouf. I am glad to use this opportunity to express my thanks to all of these gentlemen for their assistance in my studies. I wish also to express my gratitude to my fellow-students for the many courtesies I have received during the time of our association.